ADMINISTRATIVE INFORMATION

1. **Project Name:** Advanced Chlor-Alkali Technology (CPS# 1797)

2. **Lead Organization:** Los Alamos National Laboratory
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3. **Principal Investigator:** Dr. Jerzy Chlistunoff: phone (505) 667-7192,
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4. **Project Partners:** N/A

5. **Date Project Initiated:** 10/01/2001

6. **Expected Completion Date:** 9/30/2004

PROJECT RATIONALE AND STRATEGY

7. **Project Objective:**

This project focuses on the development of energy efficient chlor-alkali technology. By replacing hydrogen-evolving cathode with oxygen-consuming cathode in state-of-the-art membrane cell, the operating cell voltage and thus energy consumption can be reduced by 30%. Since the efficient cell operation requires optimum performance of all the cell components, the following issues are being addressed: (i) oxygen cathode structure and composition, (ii) anode structure, (iii) ion-exchange membrane, and (iv) operating conditions.

8. **Technical Barrier(s) Being Addressed:**

Among three chlor-alkali technologies currently in use in the United States, the membrane process is the cleanest and most energy efficient. The technology has been fully optimized and no major energy savings can be achieved by its further modifications. Replacement of hydrogen-evolving cathode with oxygen-consuming cathode is the only way to achieve substantial energy savings.

In order to become a practical alternative to the hydrogen-evolving cathode, an oxygen-consuming cathode has to meet specific criteria, such as: (i) high catalytic activity, i.e., low overpotential of oxygen reduction, (ii) efficient transport of water and oxygen to the reaction site, (iii) efficient removal of sodium hydroxide from the catalyst layer, (iv) durability, and (v) low cost. In addition, application of the oxygen-consuming cathode imposes additional requirements for the anode and membrane performance.

The major technical barriers originate from conflicting tasks that have to be performed by cell components:

- Efficient transport of liquids (water, sodium hydroxide solution) to/from the reaction site is facilitated by capillary forces, when the electrode pores are hydrophilic, whereas hydrophobic pores promote transport of oxygen

- Zero-gap configuration of the anode minimizes anode contribution to the cell resistance, but increases membrane blinding effect by chlorine gas
- An unwanted phenomenon of flooding of the cathode with sodium hydroxide and the cell resistance are minimized in a zero-gap cathode configuration, i.e., when the cathode remains in contact with the membrane, which hinders transport of hydrated sodium cations through the membrane
- Highest catalytic activity towards oxygen reduction is exhibited by noble metals that are expensive
- Significant degree of utilization and thus relatively low cost of a noble metal catalyst is achieved by using highly dispersed carbon as a support for the catalyst, whereas carbon-supported noble metal catalysts are unstable under open circuit conditions due to carbon corrosion. Moreover, carbon support contributes to generation of unwanted byproduct peroxide.
- Majority of inexpensive construction materials used for hydrogen-evolving chlor-alkali cell are incompatible in oxidizing environment of the cathode compartment of oxygen-consuming cell

9. Project Pathway:

In order to make the new technology attractive, an effort was undertaken to achieve such performance characteristics of the oxygen-depolarized cells that would match or exceed current industrial standards for hydrogen-evolving membrane cells. The following general tasks determine the overall strategic approach for the project:

- Determining factors leading to performance losses of an oxygen-consuming cell
- Studying effects of factors that affect overall cell performance, such as:
  - cell design
  - materials for the cathode and other cell components, e.g., membrane
  - operating conditions
- Optimization of cell components and operating conditions

10. Critical Technical Metrics:

Baseline Metrics (large industrial membrane cells with hydrogen-evolving cathodes at standard industrial current density of 0.4 A/cm^2):

- Cell voltage increase ≤0.1 mV/day
- Current efficiency ≥96%
- High product purity (60 ppm chloride in solid NaOH)
- Cell voltage of ~3.2 V
- Current density 0.4 A/cm^2 (effort to increase throughput undertaken)
- High durability

Project Metrics (laboratory scale cells with oxygen-consuming cathodes):

- Cell voltage increase ~0.2 mV/day (at 1.0 A/cm^2)
- Current efficiency ≥96% (at standard industrial throughput of 0.4 A/cm^2) and ≈ 92% at 2.5 times higher throughput (1.0 A/cm^2)
- High product purity (90 ppm chloride in solid NaOH)
- Cell voltage of ~1.9 V at 0.4 A/cm^2 and ~2.4 V at 1.0 A/cm^2
- Current density 1.0 A/cm^2
- Catalyst loss under open circuit conditions

PROJECT PLANS AND PROGRESS

11. Past Accomplishments:

This project is the continuation of a previous project funded by the Office of Industrial Technologies that terminated in 2000. The major accomplishments achieved under the previous program include:

- Elimination of membrane delamination upon introducing fuel cell hardware
- Three months of stable cell operation at high throughput (2.5 times higher than industrial standard) upon introducing LANL proprietary cathode flow field
- Improvement and stabilization of caustic current efficiency at around 90% at high throughputs

Under the current ITP-IMF program the project partners have:

- Significantly reduced generation of unwanted byproduct peroxide
- Eliminated cathode hardware corrosion problems
- Increased caustic current efficiency to ≥96% at standard industrial throughputs (0.4 A/cm^2) and to ~92% at high throughputs (1.0 A/cm^2)
- Critically evaluated different ion exchange membranes

12. Future Plans:

The major tasks to be accomplished in the remainder of the project include:

- Identification of unsupported catalysts of highest performance – completion 6/30/04, deliverable: report
- One month life test of unsupported catalyst of highest performance – completion 6/30/04, deliverable: report
- Extended testing of the cathode structure that provides best performance stability or evaluation of alternative ways to improve it – completion 9/30/04, deliverable: report

13. Project Changes:

Withdrawal of an industrial partner from collaboration at the end of the second project year led to loss of purified brine supply. The brine supply from a major chlor-alkali manufacturer was eventually reinstated. A new partner, Texas Brine Company, has arranged with a major chlor-alkali producer to purchase membrane quality brine in relatively small quantities required by the project. However, the resultant delay led to modifications of the project schedule. A few tasks of relatively lesser importance have been abandoned or assigned a conditional status, whereas period of time allocated for critical tasks aimed at developing cathodes containing unsupported catalysts has been reduced. Suitability of these cathodes is currently evaluated.

14. Commercialization Potential, Plans, and Activities:

Yearly production of chlorine in the United States approaches 13 million tons. Currently, only 18% of chlorine is produced using the most energy efficient membrane technology, while the remaining 82% is split between diaphragm (70%) and mercury (12%) technologies. Energy savings of at least 30% are expected from replacing hydrogen-evolving cathodes in state-of-the-art membrane cells by oxygen-consuming cathodes. More significant savings are expected from replacement of diaphragm and mercury cells by oxygen-consuming membrane cells.

Due to a relatively low cost of electrical energy and relatively unrestrictive environmental regulations in the U.S. as well as high capital investment associated with implementation of a new technology, there is no immediate interest of the domestic industry in the new energy efficient chlor-alkali process. On the contrary, a significant effort to develop chlor-alkali technology with oxygen-consuming cathode has already been made in Europe and Japan, where the energy prices are higher and environmental regulations stricter than in the United States. The domestic chlor-alkali companies are not willing to invest in the future technology unless it immediately boosts their competitiveness on the market.

Although several performance metrics of the studied technology have already matched or exceeded current industrial standards, some working characteristics of the new technology are still below current standards, e.g., performance durability. Further improvement of these characteristics is believed to be a key requirement for making the technology attractive for the industry.

15. **Patents, publications, presentations:**

1 Patent -
Patent submitted 'Oxygen-Consuming Chlor-Alkali Cell Configured to Minimize Peroxide Formation.' U.S Patent Application S.N. 10/631,073, filed 07/31/2003.

2 Publications -
2 papers in preparation

2 Presentations -
L.Lipp, S.Gottesfeld, J.Chlistunoff, *Zero-Gap Chlor-Alkali Cell With Oxygen-Consuming Cathode. Hardware Effects on the Cell Operation*, 203rd Meeting of the Electrochemical Society, Paris, France, April-May 2003
L.Lipp, S.Gottesfeld, J.Chlistunoff, *Effects of Operating Conditions on Selected Performance Characteristics of Oxygen-Depolarized Chlor-Alkali Cell.* 201st Meeting of the Electrochemical Society, Philadelphia, 2002